Quantum Design

MPMS Application Note 1014-201

Sample Mounting Considerations

There are a few important considerations for the sample holder design when mounting a sample for measurement in a magnetometer. The sample holder can be a major contributor to the background signal. Its contribution can be minimized by choosing materials with low magnetic susceptibility and by keeping the mass to a minimum.

The materials used to hold a sample must perform well over the temperature range to be used. In a gradiometer-type magnetometer, like the Quantum Design Magnetic Property Measurement System (MPMS), the geometric arrangement of the background and sample is critical when their magnetic susceptibilities will be of similar magnitude. Thus, the sample holder should optimize the sample's positioning in the magnetometer. A sample should be mounted rigidly in order to avoid extraneous sample motion during measurement. A sample holder should also allow easy access for mounting the sample, and its background contribution should be easy to measure.

This advisory introduces some mounting methods and discusses some of the more important considerations when mounting samples for the MPMS magnetometer. Keep in mind that these are only recommendations, not guaranteed procedures. The researcher is responsible for assuring that the methods and materials used will meet experimental requirements.

Measuring with a Gradiometer—Geometric Considerations

To minimize background noise and stray field effects, the MPMS magnetometer pick-up coil takes the form of a second-order gradiometer. An important feature of this gradiometer is that moving a long, homogeneous sample through it produces no signal as long as the sample extends well beyond the ends of the coil during measurement. For this reason, a drinking straw (a lightweight homogeneous plastic tube) is frequently used as a sample holder.

As a sample holder is moved through the gradiometer pickup coil, changes in thickness, mass, density, or magnetic susceptibility produce a signal. Ideally, only the sample to be measured produces this change. However, real samples usually require mounting to a sample holder, which has materials that will contribute a background signal. It is important to design a sample holder that will provide a minimal background and, even more importantly, allow the background contribution to be measured.

A homogeneous sample that extends well beyond the pick-up coils does not produce a signal, yet a small sample does produce a signal. There must be a crossover between these two limits. The sample length (along the field direction) should not exceed 10 mm in order to obtain the most accurate measurements. It is important to keep the sample susceptibility constant over its length, otherwise distortions in the SQUID signal (deviations from a dipole signal) can result. It is also important to keep the sample close to the magnetometer centerline to get the most accurate measurements.

When the sample holder background contribution is similar in magnitude to the sample signal, the relative positions of the sample and the materials producing the background are important. If there is a spatial offset between the two along the magnet axis, the signal produced by the combined sample and background can be highly distorted and will not be characteristic of the dipole moment being measured.

Even if the signal looks good at one temperature, a problem can occur if either of the contributions are temperature dependent. **Figure 1** shows a temperature dependence plot for the magnetic moment of 1) a sample with a temperature dependent susceptibility, 2) a temperature independent background, and 3) their combination.

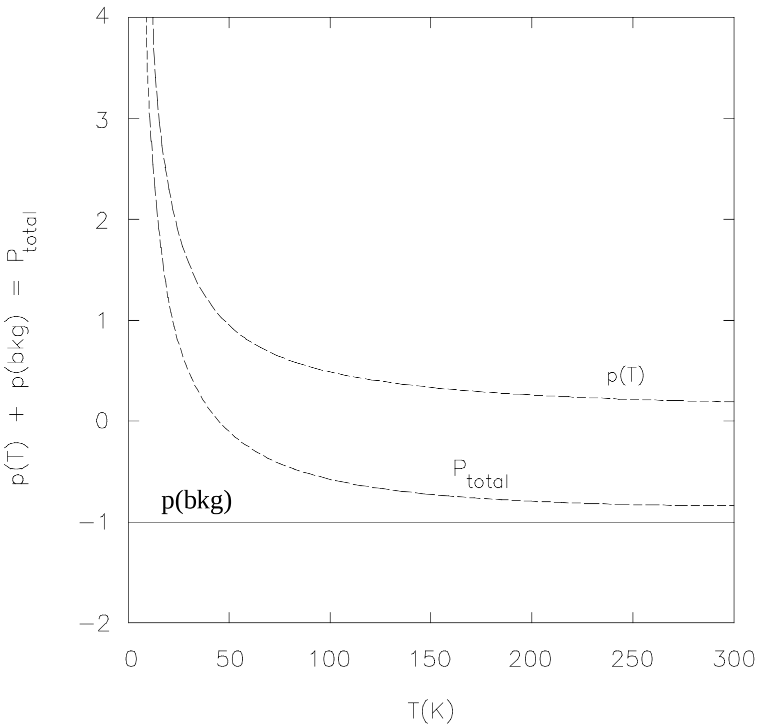


Figure 1. Moment as a function of temperature for a sample with Curie dependence p(T), a temperature independent background p(bkg), and the total moment P_{total}. When P_{total} = 0 the ration p(T)/p(bkg) = 1.

The SQUID signals for a system in which the background is displaced from the sample by 1 mm along the magnet axis are shown in **Figure 2**.

Notice that the signal no longer resembles the signal from the normal "dipole moving through a second order gradiometer" when these spatially offset signals become of comparable magnitude. It is difficult for the signal analysis routines to extract reasonable moment values from these distorted signals. Careful sample positioning and a sample holder with a center, or plane, of symmetry at the sample (i.e. materials distributed symmetrically about the sample, or along the principal axis for a symmetry plane) helps eliminate problems associated with spatial offsets.

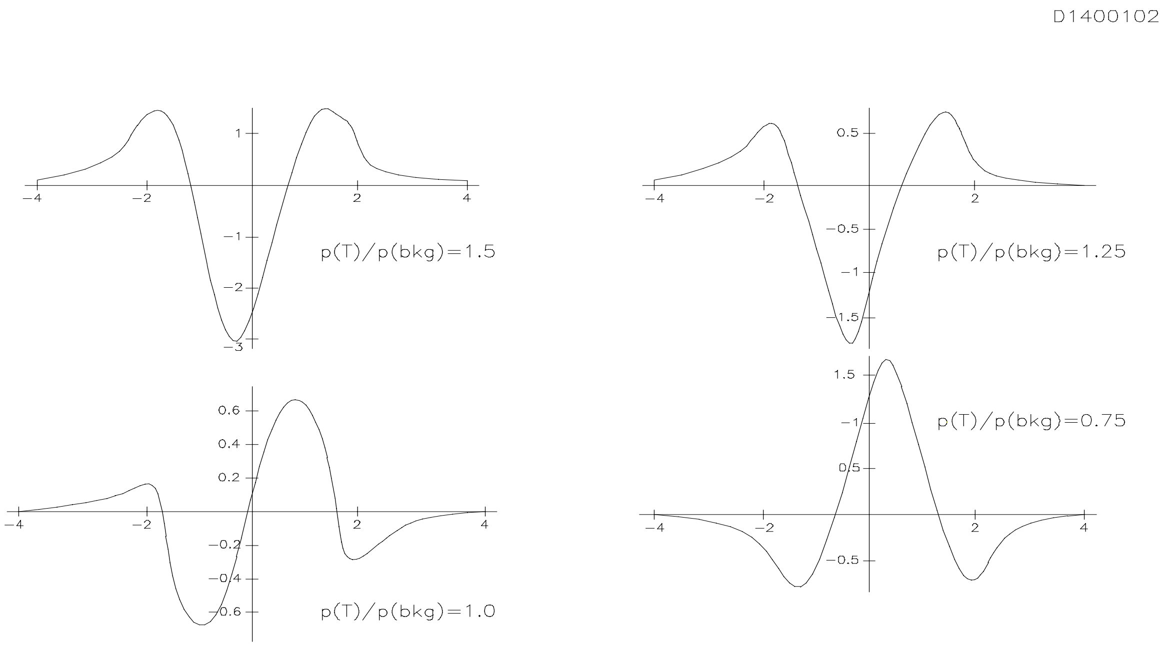


Figure 2. The calculated SQUID output signal for different values of the ratio p(T)/p(bkg) when p(T) is separated from p(bkg) by 1 mm along the axis of the gradiometer. A serious distortion of the signal is evident when p(T)/p(bkg) = 1. This distortion will result in the calculation of a non-zero value for P_{total} when p(T)/p(bkg) = 1. This separation also causes similar calculation errors for signals near $P_{total} = 0$.

Containing the Sample

Keep the sample space of the MPMS magnetometer clean and free of contamination with foreign materials. Avoid accidental sample loss into the sample space by properly containing the sample in an appropriate sample holder. In all cases it is important to close the sample holder tube with caps in order to contain a sample that might become unmounted. This helps avoid sample loss and subsequent damage during the otherwise unnecessary recovery procedure. Position caps well out of the sample-measuring region and introduce proper venting (as described below).

Powdered samples pose a special contamination threat, and special precautions must be taken to contain them. If the sample is highly magnetic, it is often advantageous to embed it in a low susceptibility epoxy matrix like Duco cement. This is usually done by mixing a small amount of diluted glue with the powder in a suitable container such as a gelatin capsule. Potting the sample in this way can keep the sample from shifting or aligning with the magnetic field. In the case of weaker magnetic samples, measure the mass of the glue after drying and making a background measurement. If the powdered sample is not potted, seal it into a container, and watch it carefully as it is cycled in the airlock chamber.

Removing and cleaning the airlock is much simpler than warming up the system to remove and clean the sample chamber. Gelatin capsules have susceptibilities of about 10^{-7} emu/Oe•g with a typical capsule having a mass of about 50 mg. These capsules are hygroscopic (easily absorb water from the atmosphere), so accurate mass measurements can be difficult to achieve. Fill the capsule with the powder, closed, and add a small drop of cement to hold the capsule together during measurements. If the capsule is not full, it may produce spatial offset problems (background-sample positioning problems) as a result of sample density inhomogeneity.

Pressure Equalization

The sample space of the MPMS has a helium atmosphere maintained at low pressure of a few torr. An airlock chamber is provided to avoid contamination of the sample space with air when introducing samples into the sample space.

By pushing the purge button, the airlock is cycled between vacuum and helium gas three times, then pumped down to its working pressure. When the green "ready" light on the front of the TCM lights up, the sample space is at working pressure. Note that if the light does not light up there is probably a leak in the interlock chamber.

During the cycling, it is possible for samples to be displaced in their holders, sealed capsules to explode, and sample holders to be deformed. Many of these problems can be avoided if the sample holder is properly ventilated. This requires placing holes in the sample holder, out of the measuring region that will allow any closed spaces to be opened to the interlock chamber.

Radial Centering

When using a second order gradiometer, measurement accuracy is dependent on the sample's radial position—how well it is positioned along the gradiometer centerline. Radial centering can be improved by placing guides at the ends of the sample tube, well out of the measuring region. See **Figure 3**.

Guides can be provided by wrapping cellophane tape around the tube to build it up to the correct diameter or by gluing on a machined cylindrical guide of low susceptibility. The sample bore is about 9 mm, so to avoid having the spacers hang up during sample holder insertion or extraction, the guides should not exceed 8 mm in diameter.

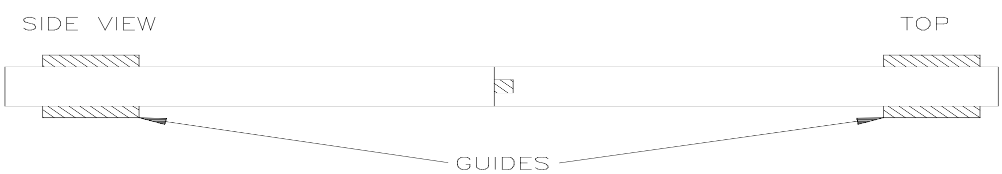


Figure 3. Place guides at the ends of the sample holder to improve radial positioning**.** Use spacers to keep the sample on the centerline

Sample Tube Connection to Sample Rod

There are several convenient methods for attaching the sample tube to the sample rod. One method is to place a spacer on the rod and attach the tube to the spacer with tape. See **Figure 4**. Another simple method is to puncture the tube with a wire that runs through the hole in the bottom of the sample rod.

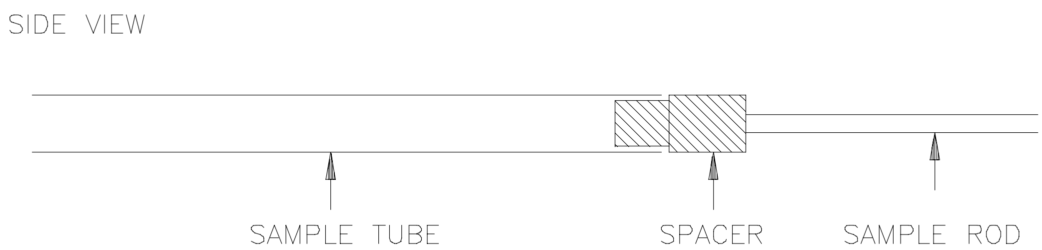


Figure 4. A method for attaching the sample tube to the sample rod.

Sample Preparation Workspace

Work area cleanliness and avoiding sample contamination are very important concerns. There are many possible sources of contamination in a laboratory, the most likely being bench tops or tools contaminated with magnetic material from previous use. A less likely but real threat comes from the magnetic dust produced in the corrosion of a building's air vents.

Use diamond tools when cutting hard materials. Avoid carbide tools because of potential contamination by the Cobalt binder found in many carbide materials. The best tools for preparing samples and sample holders are made of plastic, Titanium, brass, and Beryllium Copper (which also has a small amount of cobalt). Tools labeled non-magnetic can actually be made of steel and often be made "magnetic" from exposure to magnetic fields. However, the main concern from these "non-magnetic" tools is contamination by the iron and other ferrous metals in the tool.

It is important to have a clean white-papered workspace and a set of tools dedicated to mounting your own samples. In many cases, the materials and tools used can be washed in dilute acid to remove ferrous metal impurities. Follow any acid washes with careful rinsing with deionized water.

Example Sample Mounts

The following are specific methods for mounting samples. This is certainly not an exhaustive listing but simple suggestions to aid in your own sample holder design.

Platform Mounting

For many types of samples, mounting to a platform is the most convenient method. The platform's mass and susceptibility should be as small as possible in order to minimize its background contribution and signal distortion. In some cases it is useful to duplicate the platform on top of the sample to maintain better mirror symmetry.

Plastic Disc

A plastic disc (acid washed delrin is a suitable material) about 2 mm thick with an outside diameter equivalent to the pliable plastic tube's diameter (a clear drinking straw is suitable) is inserted and twisted into place. See **Figure 5a**. The platform should be fairly rigid.

Mount samples onto this platform with glue. Place a second disc, with a diameter slightly less than the inside diameter of the tube and with the same mass, on top of the sample to help provide the desired symmetry. Pour powdered samples onto the platform and place a second disc on top. The powders will be able to align with the field. Make sure the sample tube is capped and ventilated.

Crossed Threads

Make one of the lowest mass sample platforms by threading a cross of **white** cotton thread (colored dyes can be magnetic). Using a needle made of a non-magnetic metal, or at least carefully cleaned, thread some white cotton sewing thread through the tube walls and tie a secure knot so that the thread platform is rigid. See **Figure 5b**. Glue a sample to this platform or use the platform as a support for a sample in a container. Use an additional thread cross on top to hold the container in place.

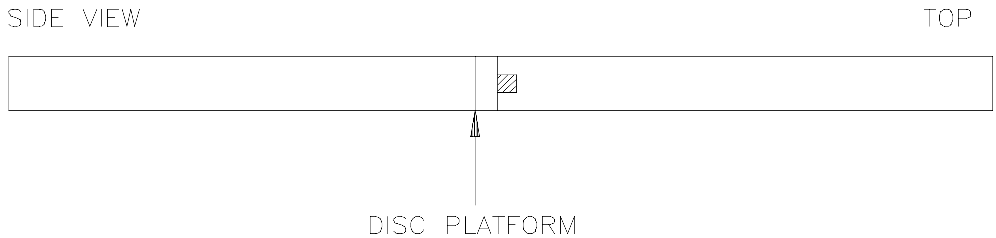
Gelatin Capsule

Gelatin capsules can be very useful for containing and mounting samples. Many aspects of using gelatin capsules have been mentioned in the section, ***Containing the Sample***. It is best if the sample is mounted near the capsule's center, or if it completely fills the capsule. Use extra capsule parts to produce mirror symmetry. The thread cross is an excellent way of holding a capsule in place.

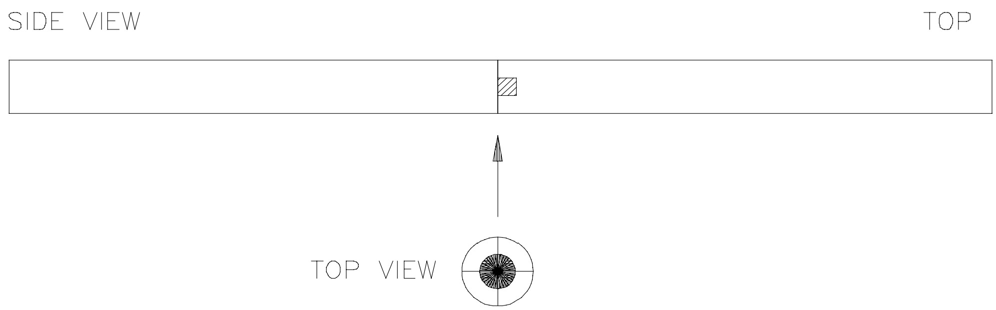
Thread Mounting

Another method of sample mounting is attaching the sample to a thread that runs through the sample tube. See **Figure 5c**. The thread can be attached to the sample holder at the ends of the sample tube with tape, for example. This method can be very useful with flat samples, such as those on substrates, particularly when the field is in the plane of the film. Be sure to close the sample tube with caps.

a) Mounting with a disc platform.



b) Mounting on crossed threads.



c) Long thread mounting.

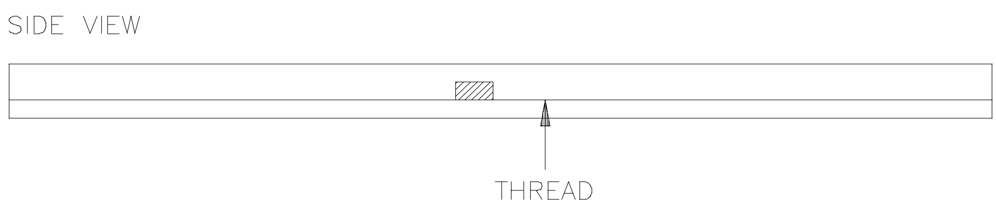


Figure 5. The use of a (a) disc platform, (b) crossed threads, and (c) thread mounting.

Air-Sensitive Samples and Liquid Samples

When working with highly air-sensitive samples or liquid samples it is best to first seal the sample into a glass tube. NMR and EPR tubes make good sample holders since they are usually made of a high-quality, low-susceptibility glass or fused silica. When the sample has a high susceptibility, the tube with the sample can be placed onto a platform like those described earlier.

When dealing with a low susceptibility sample, it is useful to rest the bottom of the sample tube on a length of the same type of glass tubing. See **Figure 6**. By producing near mirror symmetry, this method gives a nearly constant background with position and provides an easy method for background measurement (i.e. measure the empty tube first, then measure with a sample). Be sure that the tube ends are well out of the measuring region.

When going to low temperatures, check to make sure that the sample tube will not break due to differential thermal expansion. Samples that will go above room temperature should be sealed with a reduced pressure in the tube and be checked by taking the sample to the maximum experimental temperature prior to loading it into the magnetometer. These checks are especially important when the sample may be corrosive, reactive, or valuable.

Figure 6. An arrangement for measuring either an air sensitive sample or a liquid sample sealed in a tube.

Oven Option Sample Mounting

The MPMS oven option allows measurements to be made at temperatures up to 800 K (527°C). Many of the sample holder materials that are useful below 400 K are not useful to 800 K. Sample holders for the oven should be limited to a 3 mm outside diameter since the oven sample space has a 3.5 mm inner diameter. The sample rod's diameter is about 3 mm.

The following describes two methods for mounting samples for use with the oven. **Figure 7** shows a silica support rod inserted into a silica tube and fused at its end. Other materials can be used, such as brass, but the tube and rod should be of similar materials to avoid differential thermal expansion problems.

The sample is placed into the tube and on top of the rod. A second silica rod is inserted from the top, leaving a gap for the sample. Make an accurate background measurement by measuring the holder with an empty sample gap. Drill a small hole in the top rod and mount the entire arrangement to the sample rod with a piece of wire.

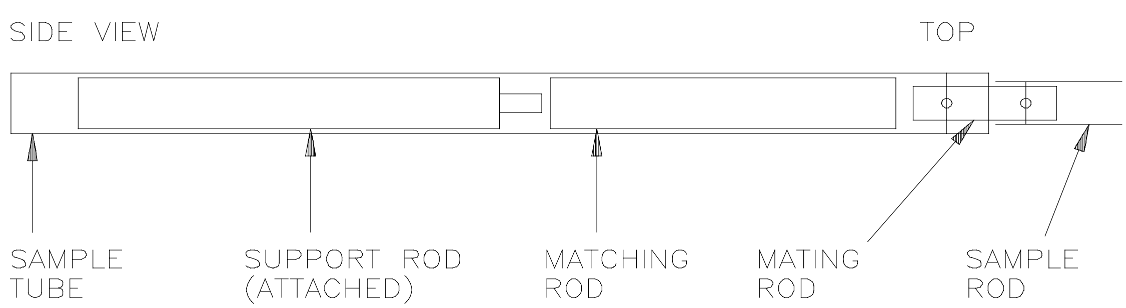


Figure 7. An arrangement for a sample mount to be used with the oven option.

Another method involves forming a constriction in silica tubing. Keep the mass of silica constant along the tube's entire length, then place the sample onto the constriction. Put the tube on the end of a sample rod and fuse. Alternatively, make several knots in a piece of suitable wire (since Platinum and Tantalum melt above 1200°C, they make good choices) and place them into the tube with a length of the wire hanging out of the tube. Collapse the silica tube above the knots to secure the tube on the wire. Use the length of wire hanging out to attach the sample holder to the sample rod.

Recovering Lost Samples

Occasional sample loss was anticipated during MPMS design. As the temperature of the sample region is raised, the full length of the sample chamber is heated to nearly the temperature of the measuring region.

To recover a sample, set the measuring temperature to 300 K and allow the sample chamber to equilibrate for at least one-half hour. Attach a suitable adhesive material to a plastic or metal tube (or rod) less than 6 mm in diameter and greater than 1 meter in length. Suitable adhesive materials include double-stick tape, plasticine, modeling clay and others. Open the vent valve, then open the chamber airlock valve. Probe the sample space until all portions of your sample have been recovered. This may require replacing the adhesive material several times.

In the event that a powder sample is lost in the sample space, a more serious cleaning may be in order. This may require warming the entire magnetometer system to room temperature and swabbing the sample space with solvent saturated cloths. Contact your Quantum Design service representative before placing any solvents or corrosive chemicals into the MPMS sample space.

Background Subtraction

Taking into consideration the various sample mounting techniques that are available to you, the background response can be manually subtracted from the total response on the MPMS (see Application Note 1014-213). Or, the background response can be collected and automatically subtracted from the total response by using the Automated Background Subtraction feature in the MPMS MultiVu software.

References

For information on specific low-susceptibility materials see the following references.

J. L. Salinger and J. C. Wheatley, *Review of Scientific Instruments* 32, 872 (1961).

J. M. Lockhart, R. L. Fagley, L. W. Lombardo, and B. Muhlfelder, *Physica B* 165&166, 147 (1990).